The Chemical Engineering of Poison Gas Manufacture

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This article is not written with the intention of adding anything to the sum total of the knowledge concerning the manufacture of toxic gases. It is merely intended to discuss the engineering features involved, for the sake of Chemical Engineering itself.

The Chemical Plant at Edgewood Arsenal, Edgewood, Md., required an expenditure of some millions of dollars and necessitated the erection of about twenty steel building averaging perhaps 50x120 feet, not counting a large machine shop, warehouse, office building, laundry, a dozen large barracks for sixteen hundred men, several miles of railroad track and all the water supply lines, electric power lines, steam lines, sewage lines and all the multitude of things to go with an enterprise of this size for the production of material and the care of men.

Such a large installation of equipment, of a sort practically never used before, does not come into existence like Topsy who "just growed," but requires a complete organization from the beginning. It was therefore necessary to build up an organization which ultimately comprised ninety officers and sixteen hundred soldiers. The routine construction of steel buildings, digging of ditches, building of roads and railroads was carried out by contractors using civilian labor. The technical organization comprised first: the Commanding Officer's Office; second, the Chemical Technology Section; third, the Procurement Section; fourth, the Traffic Section; fifth, Property Section; sixth, Construction Section; seventh, Maintenance Section; eighth, Military Section; ninth, Phosgene Production; eleventh, Mustard Production Station. The Maintenance Section also acted as Design Section working with the other sections. Each section was in charge of an experienced commissioned officer brought into the service, for just this kind of work, from civilian life. The really notable success of the Chemical Plant was due to the unfailing, hard working and courageous cooperation between the heads of the various sections, and of course to the splendid courage and staying qualities of the soldiers who worked in this most disagreeable and dangerous of all plants.

As intimated above three toxic gases were made at this plant, Phosgene, Chloropicrin and Mustard. And the engineering problems were of course too numerous and complex to more than mention them here.

Phosgene.—Phosgene is a gas condensing at 8°C and is made by a catlytic reaction between carbon monoxide and gaseous chlorine, extremely porous carbon being the catalyst. The product is $COCl_2$ and is extremely poisonous, consequently all pipes, valves and fittings had to be extraordinarily tight. To make this substance it was or course necessary to handle large quantities of liquid chlorine, more in fact than was ever dreamed of before, and to gasify it and to transport the gas in pipes in such a way as to keep the liquid and gaseous chlorine under easy control. It was necessary to design and have built, special tanks for the storage of liquid chlorine, vaporizer for vaporizing the chlorine and to install extra heavy pipe and special fittings to handle the liquid and gaseous chlorine. All this involved a good many calculations based on vapor pressure, latent heat of vaporization and density of chlorine liquid and gas. The results were very satisfactory.

The production of reasonably pure carbon monoxide had never been a commercial process until this plant was built and after a great deal of thought on the subject it was finally decided that it would be necessary to make use of the two following reactions going on simultaneously:

$2C+O_2=2CO+58{,}000$ calories and
$C+CO_2=2CO—39{,}000$ calories.

The first reaction could not be conveniently used alone on account of the enormous temperature produced by the reaction endangering the safety of the producer. The second reaction could not be conveniently used alone since it is endothermic and would soon smother the fire, requiring a frequently reversing procedure with resultant low purity of gas. Upon calculation it is found that when making proper allowance for radiation heat-loss the above reactions when going on simultaneously should produce a state of fairly constant temperature when thirty cu. ft. of oxygen is used with fifty cu. ft. of carbon dioxide. It was expected that when using seventy-hour foundry coke as the source of carbon that a carbon monoxide gas of 98% purity could be obtained.

With these basic plans it then became necessary to design a carbon monoxide plant which included an Oxygen Plant, a Carbon Dioxide Plant and a Carbon Monoxide Plant. Although such a plant had never been built, the basic ideas could not be doubted and, in full faith, the designs were rapidly pushed and the buildings and equipment purchased. Two complete 100,000 cu. ft. per day Claude liquid-air oxygen plants were erected, three complete Carbondale Machine Company's 100,000 cu. ft. per day carbon dioxide plants were erected and eight 6 ft. modified water-gas producers were erected. This equipment required the erection of five large steel buildings.

The size of this equipment was calculated on the following basis: It was required that preparation be made for eighty tons of Phosgene per day. This would require the daily production of about 650,000 cu. ft. of CO counting losses, etc., or about 8 cu. ft. per second. Knowing the amount of time which carbon dioxide must remain in contact with hot carbon at 1200°C to be completely reduced to CO and knowing the percentage of voids in a vessel filled with ordinary first sized coke it is easy to figure how fast it will be possible to pass carbon dioxide and oxygen through a 6 ft. diameter producer without allowing more than 2% of carbon dioxide to be in the gas leaving the producer. On the basis of these figures it was found that it would be necessary to have six producers with two more as stand-bys. 650,000 cu. ft. of CO gas requires the use of 235,000 cu. ft. of CO_2 and 141,000 cu. ft. of oxygen, theoretically, practically, of course, more is required. The CO gas carried a small amount of CO_2 which was removed by scrubbing with NaOH.

It was necessary to have a sufficient amount of CO in storage at any time so that in case of a breakdown in the Oxygen or Carbon Dioxide or Carbon Monoxide Plants there would be enough on hand to give time to properly shut down the catalyzer plants where the Phosgene was made. Therefore steel gas holders were built sufficient for two hours' supply.

Another interesting problem in design was the oxygen and CO_2 pressure regulators and holders. The oxygen and CO_2 must be dry before they enter into the producers and consequently cannot be stored in a water sealed gas holder. Therefore holders were designed and built using an oil seal, the oil being confined to an annular ring in the holder in which the dome floated.

Since the ordinary gas holder only operates with a pressure of about 4 in. of water it was necessary to calculate the gas pipes around the plant with sufficient size so that the drop in pressure between the holders and the catalyzer houses would not be too great. This led to the use of twelve-inch spiral-riveted galvanized gas pipes.

Before carbon monoxide combines with chlorine it must be thoroughly dried. Therefore it was necessary to design and erect drying towers wherein carbon monoxide could be thoroughly dried by sulphuric acid and, since in the process drying the gas the sulphuric acid becomes diluted with moisture and would eat out the iron pipes and pumps if allowed to get too diluted, a sulphuric acid concentrator was built to concentrate the acid as soon as it became diluted to a certain degree.

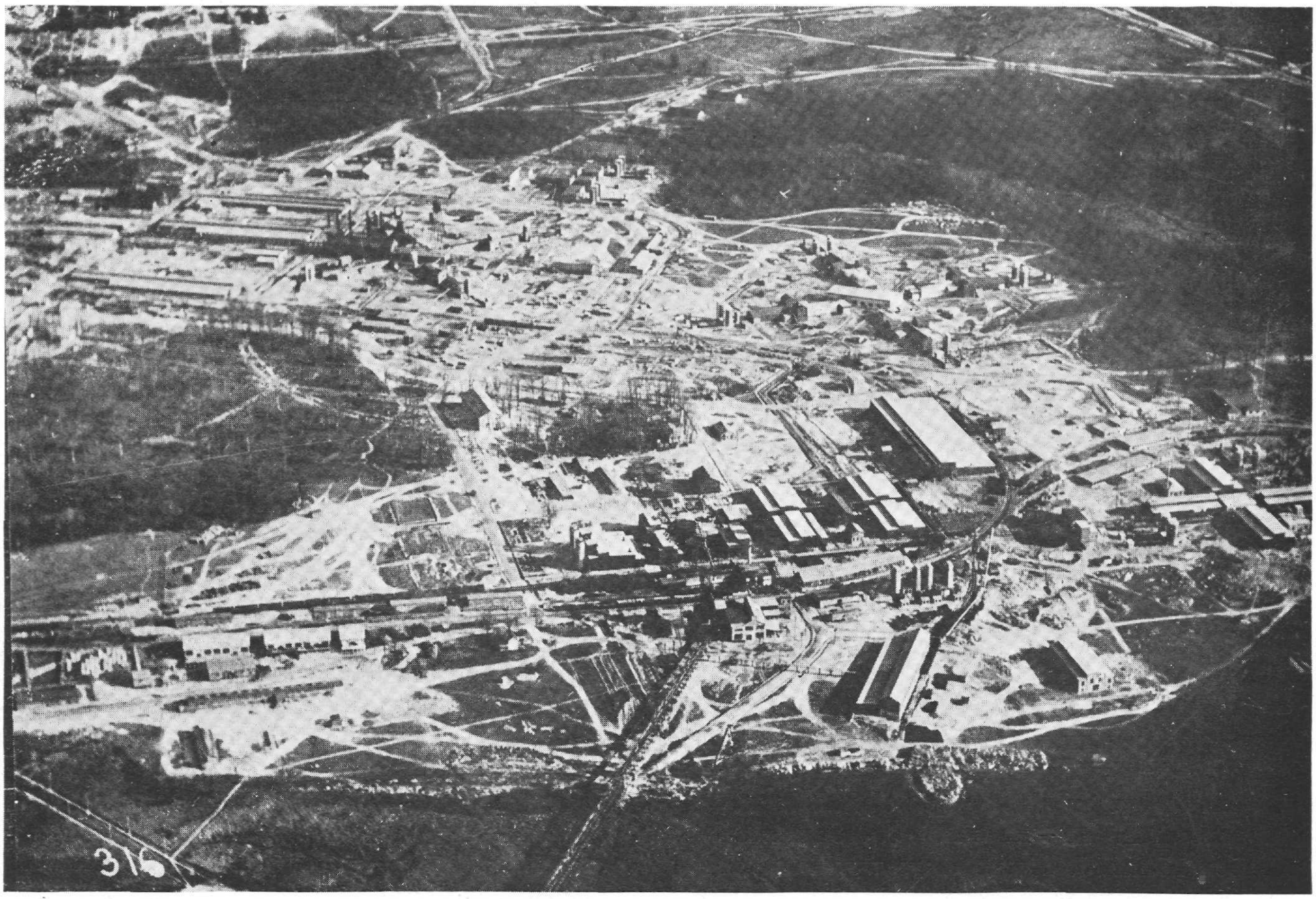
The design and construction of the catalyzer boxes was carried out on a basis of experience which one of our officers had previously had at the Oldbury Plant at Niagara Falls. To condense the Phosgene satisfactorily requires the use of a condenser working at about —10°C and to condense the maximum amount of Phosgene which the plant was designed for, required some calculations based upon the heat condensation of Phosgene. As a result of these calculations a Refrigeration Plant rated at 360 tons of refrigeration per day was erected. Special condensers in which calcium chloride brine was cooled by expanding ammonia to —10°C was kept in circulation about lead coils in which the Phosgene gas was condensed. From the condensers the Phosgene was run into large specially designed steel drums holding 1600 lbs. each.

Many of the interesting features in the Phosgene production cannot be mentioned in these brief pages.

Chloropicrin.—This Plant which was under the direction of Major Sweeney, one of our Ohio State men, was also very successful. Chloropicrin is a liquid boiling at about 115°C and is made by reaction between bleaching powder and the high explosive picric acid. Chloropicrin is a lachrymator as well as a highly toxic compound whose formula is CCl_3NO_2. The picric acid is mixed with water in a large mechanical mixer and neutralized with lime while the bleaching powder is made into a cream with water in another large mechanical mixer. These mixtures are then pumped into enormous stills about 8 ft. in diameter and 15 ft. high. Steam is introduced into the still whereupon the chloropicrin formed by the reaction between the picric acid and bleach distills over and is condensed in water cooled condensers, after which it goes into a settling tank to separate water from the heavy chloropicrin which is then ready for loading into shells or filling into drums.

The problems which required chief concern in the designing of this plant were: First, methods of handling the enormous amount of bleach (100 tons per day) required; second, methods of handling the picric acid without blowing up the plant by an explosion. We had as much as 300 tons of picric acid on hand at once. Third, calculation of, and proper arrangements for, the amount of steam required to distill the chloropicrin; fourth, calculation and design of condensers and amount of water required for the condensation of the steam and chloropicrin passing out of the still. It required about 600 H. P. of steam to produce 25 tons of chloropicrin per day.

Mustard.—Mustard is a liquid boiling at 219°C, which gives off vapors highly destructive to the mucous linings of the body and the liquid itself is terribly destructive to all living flesh that it



touches, producing fearful burns. It is made by passing ethylene gas into liquid sulfur chloride reacting according to the following equations:

$2C_2H_4+S_2Cl_2=(C_2H_4)_2SCl_2+S$

This reaction looks very simple but is exceedingly difficult to carry out practically. Sulfur chloride is a liquid easily handled and easily stored and obtainable in large quantities. Ethylene is a gas which had to be made in a plant on the grounds erected for that purpose.

To make ethylene 95% ethyl alcohol is vaporized by steam and the vapors passed through 8 in. tubes filled with kaolin in the form of sphagetti and heated from the outside to a temperature of 550°C. Under these conditions the alcohol decomposes thus:

$C_2H_5OH+heat=C_2H_4+H_2O$, about 80% of the alcohol being decomposed in the best practice yielding 97% ethylene gas, the undecomposed alcohol being condensed and recovered. It was necessary here to calculate the amount of steam necessary to vaporize the alcohol, the amount of water and condensing surface required to condense the undecomposed alcohol and water vapor and to design an alcohol still to distill and recover the alcohol passing through the ethylene furnaces undecomposed. It was also necessary to operate a water gas plant for furnishing gas to heat the ethylene furnaces. ffl

The ethylene after leaving the condenser was passed through a large scrubbing tower to remove the last traces of alcohol and ether remaining in the gas, then it was passed through especially designed sulphuric acido towers built of lead and quartz pebbles by which the ethylene was thoroughly dried, since moisture in the ethylene caused endless troubles in the mustard reaction. The ethylene gas was then compressed in reciprocating compressers, the size and power of which had, of course, to be previously calculated. From the compressers the ethylene was blown in the form of fine bubbles through the sulphur chloride in the reaction vessel.

Several varieties of reaction vessels were used and it was very difficult to secure a design whereby the difficulties resulting from the precipitation of sulphur set free in the reaction might be avoided. It must be remembered that this sulphur was mixed with "mustard" and was fearfully toxic. The reaction between ethylene and sulphur chloride is exothermic and since the temperature in the reactor must not be allowed to go over 38°C owing to the precipitation of sulphur and decomposition of 'mustard" in contact with iron at a higher temperature it was necessary to design the reactor with a sufficient amount of lead coil inside to keep the temperature of the liquid below 38°C. This was difficult owing to the tendency of sulphur to settle on the cooling pipes and make the cooling

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inefficient, notwithstanding that ice cold brine was used. If the reaction can be carried out sufficiently rapidly below 38°C the process is practical and the sulphur does not precipitate but remains in colloidal suspension.

It was necessary to install blow cases for handling sulfur chloride and for pumping the "mustard" from the reaction vesel to storage tanks and from the storage tanks into drums for shipment across the seas or for transfer to the shell filling plant. The chief difficulty at the "Mustard Plant" both in design and operation arose from the necessity for taking care of occasional bad charges in which the sulfur precipitated badly and which resulted in stoppage of pipes and gumming things up generally. The most successful way to handle this difficulty was to dissolve out the sufur mixed with "mustrd" with an excess of sulfur chloride and pump the solution by means of a special pump built for pumping liquid sulfur through a steam jacketed pipe line into a large cistern in the swamp.

The day of the armistice the Chemical Plant was regularly and smoothly producing phosgene, chloropicrin and mustard in quantities larger than shipping facilities could take it across the water and 1500 tons had accumulated stored in steel drums at the Chemical Plant.

This brief account has been written hurriedly and entirely from memory and many important and interesting phases of the work have been skipped. No time has been available nor is there space to tell of the methods used for protecting the men from the gases as much as possible, to describe the difficulties in operating such a troublesome plant twenty-four hours a day, seven days a week in three shifts per day, nor to tell of the difficulties resulting from an unwillingness of the army authorities to send us as many soldiers as we needed to properly operate the plant. Special operating difficulties, specially designed pumps, refrigerating equipment, furnaces, drying towers, reaction vessels and machines must remain undescribed but pause must be made to praise the enlisted men and subordinate officers who worked so willingly and courageously and effectively with